Study of Environmental Pollution Rustling from Balhaf Liquid Natural Gas Station Using Spectroscopy Analysis, Shabwah Governorate - Yemen

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Article Info

ABSTRACT

The present work aimed to determine the contaminants in soil resulting due to emissions that come from natural gas in the station of Balhaf which is it LNG project in Shabowah Gov, Republic of Yemen. Total 20 samples soil samples were collected at depth of approximately (0-10 cm) from different locations from the Balhaf natural gas station. These samples were analyzed by Laser Breakdown Plasma Spectroscopy (LIBS) to determine the samples toxic elements. The components of the toxic elements present in the soil samples were further confirmed by spectroscopic technique induced coupled plasma (ICP) and Fourier Transform Infrared spectroscopy (FTIR) techniques. The LIBS spectra showed the presence of different amounts of elements, including radioactive and toxic elements such as (Ac, Pu, Th, U) and (Al, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Tl, Zn), in all of the soil samples. The concentrations of the elements were calculated by ICP spectroscopy. The average concentrations of elements in the samples appeared to be 410 ppb for Al, 1.9 ppb for Ba, 2.6 ppb for Cd,2.7 ppb for Co, 2.3 ppb for Cr, 257 ppb for Cu, 30 ppb for Mn, 6,8 ppb for Ni, 63 ppb for Th, 56 ppb for Tl and 6.1 ppb for Zn, but these values did not exceed normal levels for these elements in earth crust according to reference values such as ATSDR 2020, IAEA, 200. The presence of a high concentration of toxic elements in the soil around the natural gas facility, that indicates the presence of emissions from this facility that leads to the accumulation of these elements in the soil.

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1. INTRODUCTION

Contaminants are defined as inputs of alien and potentially toxic substances into the environment; not all contaminants cause pollution, as their concentrations may be too low. Pollutants are defined as

anthropogenically introduced substances that have harmful effects on the environment [1]. Generally, environmental pollution is the contamination of air, water, or food in such a manner as to cause real or potential harm to human health or well-being, or damage or harm nonhuman nature without justification [2]. As pollutants interact with the environment, they undergo physical and chemical changes and are ultimately incorporated into the environment. The environment acts as a continuum into which all waste materials are placed. The pollutants, in turn, obey the second law of thermodynamics: matter cannot be destroyed; it is merely converted from one form to another. Thus, taken together, how substances are added to the environment, the rate at which these wastes are added, and the subsequent changes that occur determine the impact of the waste on the environment. It is important to recognize the concept of the environment as a continuum, because many physical, chemical and biological processes occur not within one of these phases, such as the air alone, but rather at the interface between two phases such as the soil/water interface [3]. Soil is a complex amalgam, a non-renewable natural resource because it cannot be re-created except within the context of geological timescales. It can be simply defined as the unconsolidated mineral or organic material on the immediate surface of the Earth that serves as a natural medium for the growth of land plants [1]. Heavy metals are highly hazardous to the environment and organisms. It can be enriched through the food chain. Once the soil suffers from heavy metal contamination, it is difficult to be remediated [4]. Lesley Fleischman, *et al*. in 2016 founds that (38) counties in 21 states from the United States (US) face a cancer risk that exceeds the U.S. Environmental Protection Agency EPA's one-in-a-million threshold level of concern. 32 counties also face a respiratory health risk from toxic air emissions that exceeds EPA's level of concern (hazard index > 1); and the areas with the greatest health risk are generally located in states with the greatest amount of oil and gas infrastructure including Texas, Louisiana, Oklahoma, North Dakota, Pennsylvania, and Colorado [5]. Lisa M. McKenzie, *et al*. in 2012 found that Residents living ≤½ mile from wells are at greater risk for health effects from natural gas development (NGD) than are residents living >½ mile from wells. Sub-chronic exposures to air pollutants during well completion activities present the greatest potential for health effects. The subchronic non-cancer hazard index (HI) of 5 for residents ≤½ mile from wells was driven primarily by exposure to trimethylbenzenes, xylenes, and aliphatic hydrocarbons. Chronic HIs were 1 and 0.4. for residents ≤½ mile from wells and >½ mile from wells, respectively. Cumulative cancer risks were 10 in a million and 6 in a million for residents living ≤½ mile and >½ mile from wells, respectively, with benzene as the major contributor to the risk[6]. In 2016, L. Blair Paulik, *et al*. investigated the impact of natural gas extraction on polycyclic aromatic hydrocarbons PAH levels in ambient air. They found that natural gas extraction, often referred to as "fracking," has increased rapidly in the U.S. in recent years. To address potential health impacts, passive air samplers were deployed in a rural community heavily affected by the natural gas boom. Samplers were analyzed for 62 polycyclic aromatic hydrocarbons (PAHs). Results were grouped based on distance from each sampler to the nearest active well. PAH levels were highest when samplers were closest to active wells. Additionally, PAH levels closest to natural gas activity were an order of magnitude higher than levels previously reported in rural areas. Sourcing ratios indicate that PAHs were predominantly petrogenic, suggesting that elevated PAH levels were influenced by direct releases from the earth. Quantitative human health risk assessment estimated the excess lifetime cancer risks associated with exposure to the measured PAHs. Closest to active wells, the risk estimated for maximum residential exposure was 2.9 in 10,000, which is above the U.S. EPA's acceptable risk level. Overall, risk estimates decreased 30% when comparing results from samplers closest to active wells to those farthest. This work suggests that natural gas extraction may be contributing significantly to PAHs in air, at levels that are relevant to human health [7].

Theo Colborn, *et al*. in 20 Sep 2011 showed that natural gas recovery technology depends on undisclosed species and quantities Toxic chemicals. A list of 944 products containing 632 chemicals used during natural gas operations was compiled. Literature searches were conducted to determine potential health effects of the 353 chemicals identified by chemical abstract service (CAS) numbers. More than 75% of the chemicals could affect the skin, eyes, and other sensory organs, and the respiratory and gastrointestinal systems. Approximately 40–50% could affect the brain/nervous system, immune and cardiovascular systems, and the kidneys; 37% could affect the endocrine system; and 25% could cause cancer and mutations. These results indicate that many chemicals used during the fracturing and drilling stages of gas operations may have long-term health effects that are not immediately expressed. In addition, an example was provided of waste evaporation pit residuals that contained numerous chemicals on the comprehensive environmental response, compensation, and liability act (CERCLA) and emergency planning and community right-to-know act (EPCRA) lists of hazardous substances [8]. Frederica Perera, in 2017 reported that fossil-fuel combustion by-products are the world's most significant threat to children's health and future and are major contributors to global inequality and environmental injustice. The emissions include a myriad of toxic air pollutants and carbon dioxide (CO_2), which is the most important human-produced climate-altering greenhouse gas. Synergies between air pollution and climate change can magnify the harm to children. Impacts include impairment of cognitive and behavioral development, respiratory illness, and other chronic diseases—all of which may be "seeded" in utero and affect

health and functioning immediately and over the life course [9]. Most of the previous studies in the natural gas sector and its impact on environmental pollution were focused on air analysis upon estimates of pollutant emissions using meteorological and emission data [10][11]. Despite the rapid expansion in natural gas extraction and production, there are not studies on the impact of residual pollution in soil surrounding natural gas plant on the environmental and health impacts these processes might have. This paper was study of pollution from the effect of natural gas in the station of Balhaf, Yemen.

2.   RESEARCH METHOD

2.1 Study Area (Balhaf) and Soil Sampling

Soils were sampled from the vicinity of the Liquid natural gas (LNG) project, which is located at Balhaf in the South of Yemen on the Gulf of Aden Balhaf at Shabwah governorate of Yemen (longitude 48.1802°E, latitude 13.9854°N) as shown in Figure. (1). Balhaf is an industrial port town and an oasis in an area of coastal dunes in the Rudum Coastal Area of Yemen. It has palm trees and white sand, which gives way to fields of black lava and to the fishing port of Bir-Ali. Near the area of the Balhaf, there are several villages as well as the nomads, and practiced agriculture and sheep grazing, goats, and camels. The construction of the LNG facilities lasted from September 2005 to the end of 2009 [12]. The production started on 15 October 2009 [13][14]. However, the Yemen LNG plant has been shut down and stopped commercial production and exports since April 2015 because of the Yemeni civil war.

20 soil samples were collected from Inside of the LNG project in Balhaf, Shabwah Governorate, Yemen, for assessment of pollution. The samples stored for analysis of metals including Ac, Al, Ba, Cd, Co, Cr, Hg, Mn, Ni, Th, Tl, Cu, Zn, Pu, U, and Pb.

Figure 1. Description of the study area showing map of Yemen and site of the LNG plant and environmental context

2.2 Characterizations

A – Inductively coupled Plasma Technique (ICP)

The inductively coupled Plasma Technique (ICP-AES) analyses of the 20 soil samples were carried out the laboratory of General Administration of Forensic Evidence (Khartoum, Sudan) using Shimadzu (ICPE-9000, Japan). In this investigation, the samples were dried at 105^C for 3 h. About 0.2 g of sample was accurately weighed into a container made of PFA (a perfluoroalkoxy polymer), which was then placed in a microwave pressure vessel. After addition of 4 ml of concentrated nitric acid and 0.5 ml of concentrated hydrofluoric acid, the samples were digested by using a microwave power progressively increasing up to 400W during 40 min. After cooling, the solutions were accurately diluted to 100 ml with water. In addition, open digestion in a glass beaker was performed with 0.5 g of sample, accurately weighed, by heating with 12 ml of aqua regia for 45 min, followed by evaporation almost to dryness. To the hot residue, 2.5 ml of concentrated hydrochloric acid and 2.5 ml of hydrogen peroxide were added, followed by accurate dilution to 50 ml with water. One replicate per digestion method was done for each sample.

B - Laser Induced Breakdown Spectroscopy Technique (LIBS) Measurement

LIBS was used to identify the heavy metals and radioactive elements which can exist in polluted soil. Soil samples were irradiated by a nitrogen laser, with an energy of 100 mJ, which is operating in the ultraviolet

range (typically 337.1 nm). This technique is based on the concept that the laser can vaporize the surface of the material and exciting its atoms or molecules with the laser pulse. The excited energy that holds the atom at the higher energy level will be released and the atoms return to their ground state. LIBS atomizes only a small portion of the sample by the focused laser pulse. Analytical process foe qualitative can be explained as following: a high-power pulsed laser sends onto the sample absorbs the energy from the laser. Sample atomize, ionizes, and forms the plasma, After the laser pulses are off, excited atoms and ions related back to the ground state, spectra emitted by the excited species is indicated the presence of atomic species at various sites in the plasma, relative abundance.

C. Fourier Transform Infrared Technique (FTIR)

The FTIR was used to identify the functional groups of soil samples. The spectra were recorded between 4,000 and 400 cm^{-1} using FTIR (FTIR-8400S, Shimadzu) with 1 cm^{-1} resolution. Pellets were prepared by mixing the soil samples with KBr. By applying sufficient pressure, the mixture is pressed into a transparent disc, the usual analyse / KBr ratio is ca. 1:100. FTIR spectra of soil samples were recorded.

3. RESULTS AND DISCUSSIONS

3.1. Inductively coupled Plasma Technique (ICP-AES) Result.

The soil samples were collected and analysed by ICP technique to determine the concentration of heavy metals (e.g., Al, Ba, Cd, Co, Cr, Cu, Mn, Ni, Th, Tl, and Zn). Aluminium (Al) levels, 410 ppb, were the highest compared with other elements as indicated in Figure (2). This amount has a lower value compared to the crustal average according to reference values such as ATSDR 1999, IAEA, 200 [15]. In addition, the results showed that the Barium (Ba) concentration is 1.9 ppb, which is lower than the crustal average [16]. Cadmium (Cd), Cobalt (Co), and chromium (Cr) are poorly concentrated in all samples, the distribution ranging from 2.3 to 2.7 ppb. The concentration of these elements did not exceed the normal concentration in crustal. Copper concentration level was found at 57 ppb, thorium (Th) was 63 ppb, Manganese (Mn) was the concentration at 30 ppb and thallium (Tl) was 56 ppb the obtained values of these elements are well below than the normal concentration in crustal. The zinc (Zn) levels was 6.1 ppb and nickel (Ni) was 6.8 ppb, which are lower than the crustal abundance [17][18][19].

Table 1. Concentrations of elements in all samples by ICP

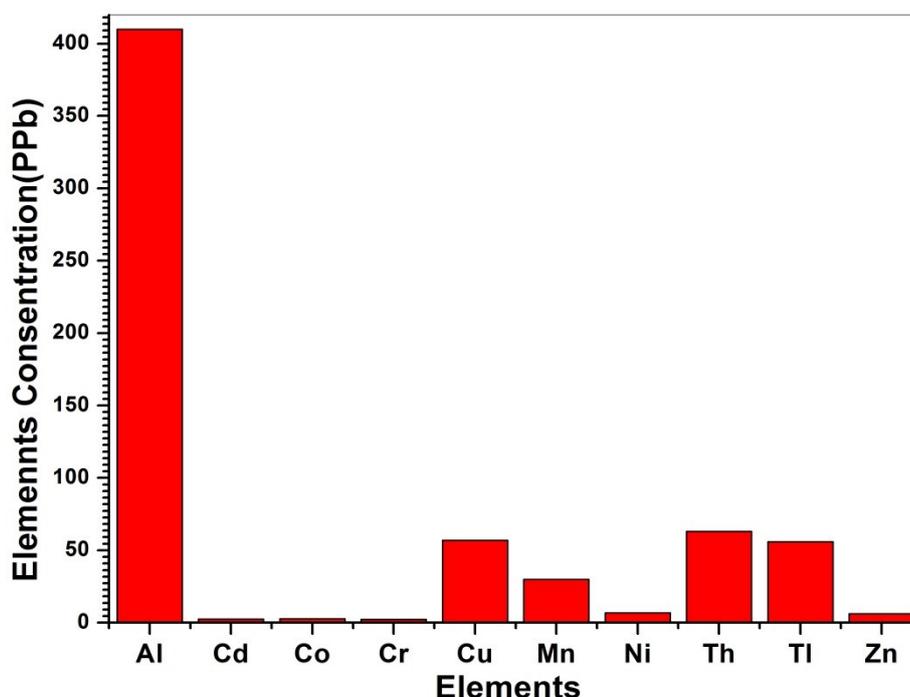| Element	Al	Ba	Cd	Co	Cr	Cu	Mn	Ni	Th	Tl	Zn
	410	1.9	2.6	2.7	2.3	257	30	6.8	63	56	6.1

Figure 2. Concentration of heavy metals and radioactive elements in soil analysed by ICP-AES spectrometer

3.2.   *Laser Induced Breakdown Spectroscopy Technique (LIBS) Result.*

For indication, after irradiation with 100 mJ pulse energy, the spectra were recorded in the region from 385 nm to 1055 nm. Atomic spectra database National Institute of standards and Technology (NIST) and Hand book of Basic Atomic Spectroscopic Data was used for the spectral analysis of the samples [20]. The obtained LIBS spectra covered wide range of the spectrum ranging from the ultraviolet (UV) region to the near-infrared (NIR) region. Figure (4) show the high intensity of elements in LIBS spectra at all samples. The identification of the elements is displayed in table (2), the spectra of the soil samples indicate the presence of different amounts of elements, including radioactive and heavy metals such as (Ac, Pu, Th, U) and (Al, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Tl, Zn), as presented in Figure (4). It is clear that from tables (2) that the Actinium ions (Ac^{+1}) appeared in one sample with low amount. Aluminium atoms appeared in some samples with low amount especially in the one sample. Barium ions (Ba^{+1}) was detected in some in samples. Cadmium atoms (Cd) appeared in three samples only with non-considerable amount. Cobalt atoms (Co) has just appeared in three samples with a low amount, additionally cobalt ions (Co^{+1}) appeared with the low amount in two samples, there are several different wavelengths for the cobalt appeared as shown in the table (2). Chromium atoms were found at a different amount, and with different wavelengths. The copper ion (Cu^{+2}) was found in all samples with a high amount compared with the previous elements. Mercury atoms (Hg) were found with the relatively little amount in fourteen samples, (this element is highly toxic even with little amount [21]. Manganese ion (Mn^{+1}) was presented with the relatively little amount in five samples. The Nickel ion (Ni^{+3}) was found in high amounts in all samples. Plutonium atoms (Pu) was found in very high amounts in all samples. Moreover, Thorium atoms (Th) were found at a different amount, not that, the wavelength (1049.282) nm appeared in all samples with relatively high amounts. Besides neutral atoms, ions of different amounts and ionization stages also were recorded. Thallium atoms (Tl) appeared in some samples with a low amount. Uranium atoms appeared in five samples with low amounts especially in sample 3, also uranium ions appeared with the low amounts in fourteen samples. The zinc atom (Zn) was found in a low amount in one sample only.
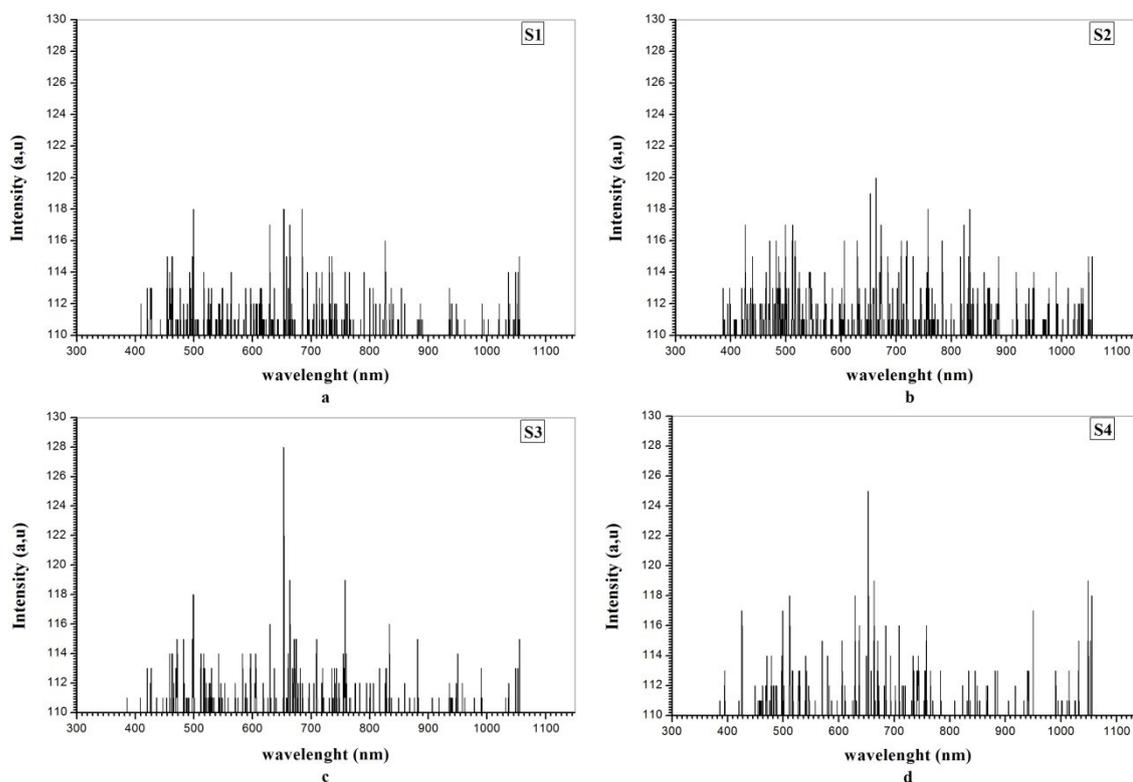

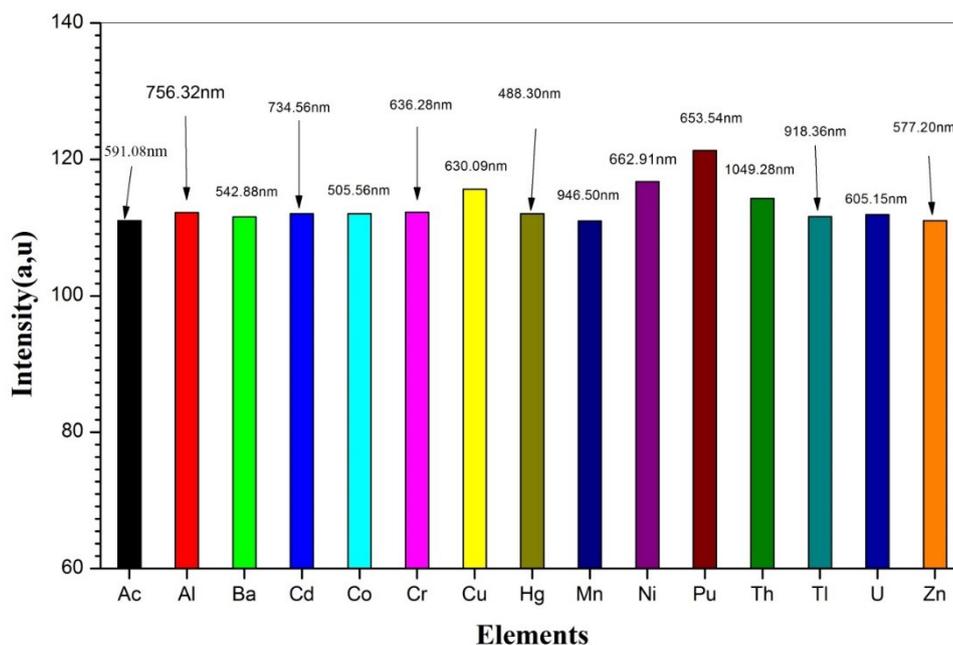Figure 3. Examples of LIBS emission spectrum of first four samples

Figure 4. Elements at high levels of samples analyzed by LIBS

Table 2. The analyzed data for heavy and radioactive elements of samples of soil irradiated with laser energy of 100 mJ.

Elements	Emission lines (nm)
Ac II	591.0856
Al I	756.3217
Al II	919.8698
Ba I	739.2541
Ba II	542.8839
Cd I	734.5653
Co I	388.526, 678.4863, 809.3998
Co II	505.5604, 692.3654, 993.2038
Cr I	385.5251, 387.0255, 411.9704, 436.9152, 453.9827, 478.9276, 500.8715, 600.4633, 609.8411, 636.2864, 721.9991, 905.99073
Cr II	736.0657, 800.022, 991.7034
Cu II	416.6593, 538.195, 630.097, 644.1637, 881.0458
Cu III	664.4196
Hg I	488.3053, 546.0723, 672.1094, 1022.8376
Hg II	496.1827, 748.6319, 975.9488
Mn I	402.5926, 415.1588, 728.3759
Mn II	873.1685, 946.5026
Ni I	443.1045
Ni IV	617.7184, 662.9192
Pu I	653.5414
Th I	399.591, 422.848, 427.537, 450.981, 463.360, 466.548, 477.427, 480.615, 485.304, 489.805, 502.372, 521.127, 530.317, 544.384, 552.261, 555.262, 556.950, 561.639, 564.640, 620.719, 628.596, 634.785, 655.041, 665.920, 694.053, 717.310, 720.498, 761.010, 803.022, 823.278, 838.845, 887.235, 949.503, 1049.282, 1055.472
Th II	394.902, 397.903, 440.103, 458.671, 483.616, 492.994, 595.774, 637.974, 650.353, 676.798, 1024.338
Tl I	837.3455, 918.3693
U I	860.7899
U II	547.5728, 605.1522
Zn I	577.2065

3.3.   *Fourier Transform Infrared Technique (FTIR) Result*

Twenty samples have been analysed by the FTIR spectrometer to investigate the presence of functional groups which can help to characterize compounds in the samples. Figure (5) shows FTIR spectra of represented soil samples. The band due to the methyl functionalities vibrated at 875 cm⁻¹ was used as a normalizing factor since no change is expected for the band of these groups. Several absorption peaks at different wave numbers were observed in the spectra of represented soil samples, shown in Table (3). The FTIR Spectrum contains the entire information about the molecular structure of the investigated samples. From the frequency and intensities of some spectral bands, it was possible to predict the kind of chemical groups present in the studied samples [22]. The results showed that the peaks around 2520 cm⁻¹ and 1430 cm⁻¹ are due to (O-H) (carboxylic acids) for most samples [23][24]. A normal range of carbonyl group (C=O) is 1800 to 1600 cm⁻¹[25]. And the results showed that a strong transmittance band was at 1800 cm⁻¹ within the range for all samples referred to as anhydrides [23].   Bands at1625 cm⁻¹, at 1430 cm⁻¹, at 775cm⁻¹ cm⁻¹ and 710 cm⁻¹ could be attributed to heterocyclic compounds (N–H), amines(NH₂) and amides(N–H) [26][23][27]. And appeared this results in all most samples as shown in the graphs from Figure (5), and table (3) and the band at 710 cm⁻¹ corresponds to Ca─O bonds [26]. In addition, C-O group which has been observed in many compounds as Alcohol, ethers, esters, carboxylic acids, and anhydrides appeared at 1020 cm⁻¹ with a strong band in all samples [23][178]. Also, the results of all samples indicated to the presence of aliphatic (C–N) stretching at 1020 cm⁻¹ [27]. The results showed analysis group Nitrate NO₂ asymmetric stretching at (710) cm⁻¹ within the range (750–650) cm⁻¹ in all samples except five samples [27]. The absorption bands at 875 cm⁻¹ attributed to the out-of-plane bending of C–H, which observed in all samples [27][28]. In the fingerprint region, vibrations of many functional groups are observed, such as phosphorus compound at 460 cm⁻¹ , and sulfur compounds at 520 cm⁻¹, these groups appeared in all samples [27]. These results are in good agreement with various data available in the literature where secondary amide N–H, nitrate NO₂ bending, C–O stretching, alcohols and phenols, C–O stretching, and C–O–H in-plane bending, these functional groups may facilitate heavy metal binding on the soil samples.
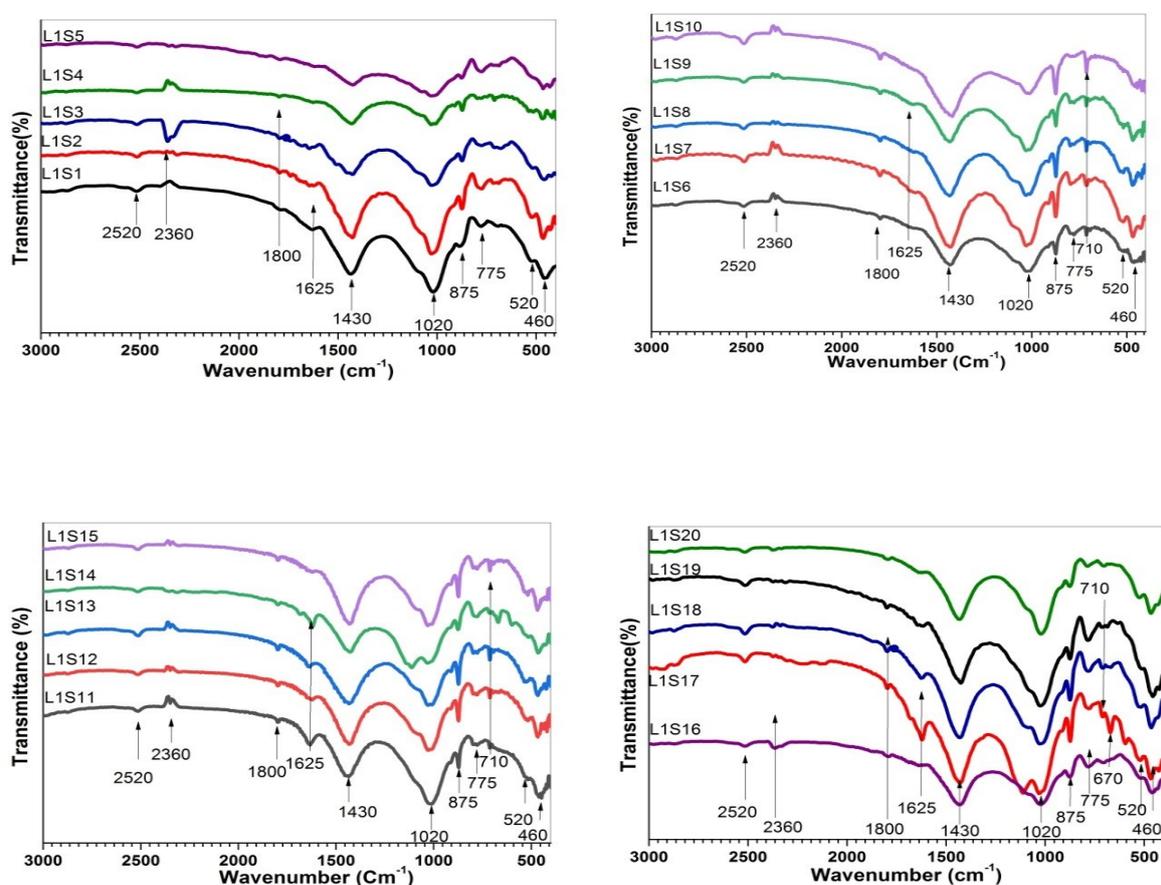

Figure 5. FTIR spectra of soil samples

Study of Environmental Pollution Rustling from Balhaf Liquid Natural Gas Station Using Spectroscopy Analysis, Shabwah Governorate - Yemen (Yosef Ahmed Yahya Alsabah)

Table 3. Various absorption peaks for the soil samples

Wave number (cm^{-1})	Assignment	Ref.	Comments
460	P–Br stretching, phosphorus compound	[27]	Observed in the spectra of all samples
520	S–S stretching, sulfur compounds	[92]	Observed in the spectra of all samples
710	Secondary amide N–H wagging, Amides. Nitrate NO2 bending, nitrogen-containing compounds. Ca-O	[27][23] [26]	Observed in the spectra of 15 samples
775	NH2 wagging and twisting, Amines	[27][23]	Observed in the spectra of all samples
875	Out-of-plane C–H bending, Aromatic Compounds	[29] [27][23][28]	Observed in the spectra of all samples
1020	C–O stretching, Alcohols and Phenols. Aliphatic C–N stretching, Amines. Si–O–Si asymmetric stretching, silicon compounds.	[27][23]	Observed in the spectra of all samples
1430	C–O–H in-plane bending, Carboxylic acids. N–H, Heterocyclic Compounds	[27][23]	Observed in the spectra of all samples
1625	N-H bend, Amides& amines	[27][23]	Observed in the spectra of 14 samples
1800	C=O stretching, Anhydrides	[23]	Observed in the spectra of all samples
2520	O-H, Carboxylic acids	[27]	Observed in the spectra of all samples

4.   CONCLUSION

This research focused on studies of soil pollution utilizing LIBS technology combined with ICP and FTIR. the search samples were soil from different inside of LNG project in Balhaf, coupled plasma technology showed the presence of the following elements (Al, Ba, Cd, Co, Cr, Cu, Mn, Ni, Th, Tl, and Zn). LIBS technology also showed the presence of a group of toxic and radioactive elements, which are as follows (Ac, Pu, Th, U) and (Al, Ba, Cd, Co, Cr, Cu, Hg, Mn, Ni, Pb, Tl, Zn). FTIR technique indicated the possibility of these items in of LNG project in Balhaf. Quantitative measurements of toxic metals have been carried out by using ICP, the results were compared with different international standards. By analyzing the results of the ICP for the samples, it is clear that the concentration of toxic elements is high. The LIBS technique showed the presence of the dangerous element the plutonium in all samples, with a higher intensity than all other elements.

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